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(54) Fuel compositions

(57) A fuel composition for use in a homogeneous charge compression ignition (HCCI) engine, comprising a gasoline base fuel and one or more additional components selected from the group consisting of (i) a diesel fuel ignition improver, (ii) a Fischer-Tropsch derived gas

oil and (iii) a Fischer-Tropsch derived naphtha fuel. Also provided are a process for preparing the fuel composition and its use in an internal combustion engine.

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Description

[0001] This invention relates to fuel compositions for use in homogeneous charge compression ignition (HCCI) engines, and to the preparation and use of such compositions.

[0002] The HCCI internal combustion engine is a hybrid of the well known spark ignition (SI, petrol) and compression ignition (CI, diesel) engines. A homogeneous, typically highly dilute, fuel/air mixture is created in the inlet system, as in a SI engine, but during the compression stroke the mixture auto-ignites as in a CI engine. Potentially HCCI engines can offer the efficiency of a diesel engine but with cleaner operation (eg, lower emissions of particulates and nitrogen oxides) and lower cyclic variations.

[0003] Various working HCCI engines have been described in the literature (see editor's keynote address (page 1) in "A new generation of engine combustion processes for the future?", Ed. P. Duret, *Editions Technip*, Paris, 2002, ISBN 2-7108-0812-9). These include the ATAC (Active Thermo-Atmospheric Combustion) (Onishi, S. et al, SAE Paper # 790501, SAE (Society of Automotive Engineers) 1979); TS (Toyota - Soken); FDCCP (Fluid Dynamically Controlled Combustion Process); AR (Activated Radicals) (Ishibashi, Y. and Arai, M., SAE Paper # 960742, SAE 1996); PCCI (Pre-mixed Charge Compression Ignition) (Ayoma, T. et al, SAE Paper # 960081, SAE 1996) and CAI (Controlled Auto-Ignition) (Oakley, A. et al, SAE Paper # 2001-01-1030, SAE 2001) engines.

[0004] HCCI combustion processes are also currently used in certain commercially available 2-stroke engines but 4-stroke engines exploiting the advantages of the HCCI technology do not yet appear to be feasible over a wide operating range.

[0005] One of the main problems with HCCI engines is that at low loads it can be difficult to ensure that auto-ignition always occurs. Olsson, Jan-Ola et al [SAE Paper # 2001-01-1031, SAE 2001] describe blending of the easily ignited fuel n-heptane with a gasoline base fuel (iso-octane) to promote auto-ignition in a HCCI engine. The n-heptane and iso-octane are metered separately into the engine under an electronic closed loop control system, so that the overall fuel formulation may be tailored in response to load conditions. This strategy may be used to extend the operating regime of a HCCI engine.

[0006] However, it is now well established that the conventional measures of auto-ignition quality in gasoline fuels - RON (Research Octane Number) and MON (Motor Octane Number) - are not relevant to auto-ignition in HCCI combustion using such fuels (see Montagne, X. et al in "A new generation of engine combustion processes for the future?", Ed. P. Duret, *Editions Technip*, Paris, 2002, ISBN 2-7108-0812-9 (page 177)). It has further been reported that the efficiency of HCCI combustion can be adversely affected in blends of gasoline with diesel fuels by poor combustion due to poor fuel vapourisation (see Oakley et al (*supra*) and Christensen, M. et al, SAE Paper # 1999-01-3679, SAE 1999). Thus it is by no means straightforward to identify gasoline fuel additives which might be used as alternatives to the n-heptane tested by Olsson et al, to improve the auto-ignition properties of the fuel and thus extend the operating regime of a HCCI engine running on it.

[0007] Additives have now however been found which, when incorporated into a gasoline base fuel, can improve its auto-ignition properties in a HCCI engine, particularly at low engine loads.

[0008] According to a first aspect of the present invention there is provided a fuel composition for use in a homogeneous charge compression ignition (HCCI) engine, the composition comprising a gasoline base fuel together with one or more additional components selected from the group consisting of (i) a diesel fuel ignition improver, (ii) a Fischer-Tropsch derived gas oil and (iii) a Fischer-Tropsch derived naphtha fuel.

[0009] It has been found that the inclusion of such components in a gasoline fuel can improve its auto-ignition capability and thus improve its performance in a HCCI engine particularly at lower loads. A HCCI engine running on a fuel composition according to the invention can therefore function at a lower load, at any given speed, than when running on the gasoline base fuel alone; the invention may thus be used to extend the operating range of the engine.

[0010] By "for use in a HCCI engine" is meant that the fuel composition is suitable for such use, whether or not it is actually intended for such use. The term "HCCI engine" is intended to encompass any engine which is operating or is operable in the HCCI mode, whether or not it is also capable of operating in another mode such as spark ignition or diesel compression ignition. In engines capable of operating in more than one such mode, the present invention can extend the operating regime over which HCCI operation is possible and/or feasible (in particular without undue misfiring).

[0011] The gasoline base fuel comprises a liquid hydrocarbon fuel and would normally be suitable for use in an internal combustion engine of the spark ignition (petrol) type. Gasolines typically contain mixtures of hydrocarbons boiling in the range from 25 to 236 °C (EN-ISO 3405), the optimal ranges and distillation curves typically varying according to climate and season of the year. The hydrocarbons in a gasoline fuel may conveniently be derived in known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons, hydro-cracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

[0012] The research octane number (RON) of the gasoline base fuel may suitably be from 80 to 100, preferably from 90 to 100, more preferably from 94 to 100 (EN 25154). Its motor octane number (MON) may suitably be from 80 to

100, preferably from 84 to 100 (EN 25163).

[0013] It may have an olefin content of for instance from 0 to 20 % v/v (ASTM D1319), an oxygen content of for instance from 0 to 5 % w/w (EN 1601), an aromatics content of for instance from 0 to 50 % v/v (ASTM D1319) and in particular a benzene content of at most 1 % v/v.

[0014] The base fuel, and suitably also the overall fuel composition, preferably has a low or ultra low sulphur content, for instance at most 1000 ppmw (parts per million by weight), preferably no more than 500 ppmw, most preferably no more than 100 or 50 or even 10 ppmw. It also preferably has a low total lead content, such as at most 0.005 g/l.

[0015] Oxygenates may be incorporated in the gasoline base fuel; these include alcohols (such as methanol, ethanol, iso-propanol, tert-butanol and iso-butanol) and ethers (preferably ethers containing 5 or more carbon atoms per molecule, eg, methyl tert-butyl ether). Such ethers may be used in amounts up to 15 % v/v of the base fuel, but if methanol is used, it can generally only be in an amount up to 3 % v/v and stabilisers may be required. Stabilisers may also be needed for ethanol, which may generally be used up to 5 % v/v. Iso-propanol may generally be used up to 10 % v/v, tert-butanol up to 7 % v/v and iso-butanol up to 10 % v/v.

[0016] Oxygenates may in particular be desirable additives in unleaded gasoline fuels, since they are of use as octane boosters.

[0017] Particularly preferred gasoline base fuels incorporate from 0 to 10 % v/v of at least one oxygenate selected from methanol, ethanol, iso-propanol and iso-butanol.

[0018] A gasoline base fuel may include one or more additives such as anti-oxidants, corrosion inhibitors, ashless detergents, dehazers, dyes and synthetic or mineral oil carrier fluids. Examples of suitable such additives are described generally in US Patent No. 5,655,629. They can be added directly to the gasoline or can be blended before addition with one or more diluents, to form an additive concentrate.

[0019] The gasoline base fuel preferably comprises a major proportion (by which is meant preferably 99 % w/w or more of the overall base fuel, more preferably 99.5 % w/w or more, most preferably 99.9 % w/w or more, even up to 100 % w/w) of liquid hydrocarbon gasoline fuel (which optionally incorporates one or more oxygenates), and a minor proportion of any additives present. The (active matter) concentration of any additives present in the base fuel is thus preferably up to 1 % w/w, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to 150 ppmw.

[0020] The diesel fuel ignition improver (i) is an ignition improving agent suitable for use in a diesel fuel composition. It may comprise one or more reagents selected from the group consisting of:

a) organic nitrates of the general formula R^1-O-NO_2 , or nitrites of the general formula R^1-O-NO , where R^1 is a hydrocarbyl group such as in particular an alkyl, cycloalkyl, alkenyl or aromatic group, or an ether containing group, preferably having from 1 to 10, more preferably from 1 to 5, carbon atoms;

b) organic peroxides and hydroperoxides, of the general formula $R^2-O-O-R^3$, where R^2 and R^3 are each independently either hydrogen or a hydrocarbyl group such as in particular an alkyl, cycloalkyl, alkenyl or aromatic group, preferably having from 1 to 10, more preferably from 1 to 5, carbon atoms; and

c) organic peracids and peresters, of the general formula $R^4-C(O)-O-O-R^5$, where R^4 and R^5 are each independently either hydrogen or a hydrocarbyl group such as in particular an alkyl, cycloalkyl, alkenyl or aromatic group, preferably having from 1 to 10, more preferably from 1 to 5, carbon atoms.

[0021] Examples of ignition improvers of type (a) include (cyclo)alkyl nitrates such as isopropyl nitrate, 2-ethyl hexyl nitrate (2EHN) and cyclohexyl nitrate, and ethyl nitrates such as methoxy ethyl nitrate. Examples of type (b) include di-tert-butyl peroxide.

[0022] Other diesel ignition improvers are disclosed in US-4,208,190 at column 2, line 27 to column 3, line 21. The diesel ignition improver (i) is preferably a (cyclo)alkyl nitrate, more preferably 2-ethyl hexyl nitrate.

[0023] Ignition improvers of this type are widely used as cetane improvers in diesel fuels, where auto-ignition can be a significant problem. They have not however been used as additives for gasoline fuels, where octane rather than cetane numbers are important.

[0024] Diesel fuel ignition improvers are commercially available for instance as HITECTM 4103 (ex Ethyl Corporation).

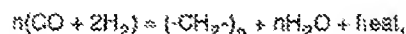
[0025] In the fuel composition of the invention, component (i) may be present in a concentration of up to 1 % v/v, preferably from 0.05 to 1 % v/v, more preferably from 0.1 to 0.7 % v/v, such as from 0.2 to 0.5 % v/v.

[0026] The Fischer-Tropsch derived gas oil (ii) is a liquid hydrocarbon middle distillate gas oil with boiling points within the typical diesel fuel range, ie, from about 150 to 370 °C. It is a reaction product of a Fischer-Tropsch methano condensation process, such as for example the process known as Shell Middle Distillate Synthesis (van der Burgt et al, "The Shell Middle Distillate Synthesis Process", paper delivered at the 5th Synfuels Worldwide Symposium, Washington DC, November 1985; see also the November 1989 publication of the same title from Shell International Petroleum Company Ltd, London, UK). Fischer-Tropsch derived gas oils are low in undesirable fuel components such as sulphur, nitrogen and aromatics and tend to lead to lower vehicle emissions. They are typically used in diesel fuel compositions,

in the form of blends with other diesel base fuels such as petroleum derived gas oils, but not in gasoline fuel compositions.

[0027] The Fischer-Tropsch derived component (ii) should therefore be suitable for use as a diesel fuel, and its components (or the majority, for instance 95 % w/w or greater, thereof) should have boiling points within the typical diesel fuel ("gas oil") range, i.e. from about 150 to 400 °C. It will suitably have a 90 % w/w distillation temperature of from 300 to 400 °C.

[0028] By "Fischer-Tropsch derived" is meant that a fuel is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic, hydrocarbons:



in the presence of an appropriate catalyst and typically at elevated temperatures (eg. 125 to 300 °C, preferably 175 to 250 °C) and/or pressures (eg. 5 to 100 bar, preferably 12 to 50 bar). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired.

[0029] A gas oil product may be obtained directly from this reaction, or indirectly for instance by fractionation of a Fischer-Tropsch synthesis product or from a hydrotreated Fischer-Tropsch synthesis product. Hydrotreatment can involve hydrocracking to adjust the boiling range (see, eg. GB-2 077 289 B and EP-A-0 147 873) and/or hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0 583 836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired gas oil fraction(s) may subsequently be isolated for instance by distillation.

[0030] Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydroreforming, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in US-A-4,125,566 and US-A-4,476,955.

[0031] Typical catalysts for the Fischer-Tropsch synthesis of paraffinic hydrocarbons comprise, as the catalytically active component, a metal from Group VIII of the periodic table, in particular ruthenium, iron, cobalt or nickel. Suitable such catalysts are described for instance in EP-A-0 583 836 (pages 3 and 4).

[0032] An example of a Fischer-Tropsch based process is the SMDS (Shell Middle Distillate Synthesis) described in "The Shell Middle Distillate Synthesis Process", van der Burgt et al (*supra*). This process produces middle distillate range products by conversion of a natural gas (primarily methane) derived synthesis gas into a heavy long-chain hydrocarbon (paraffin) wax which can then be hydroconverted and fractionated to produce liquid transport fuels such as the gas oils useable in diesel fuel compositions. A version of the SMDS process, utilising a fixed-bed reactor for the catalytic conversion step, is currently in use in Bintulu, Malaysia and its products have been used in petroleum derived gas oil blends in commercially available automotive fuels.

[0033] Gas oils prepared by the SMDS process are commercially available for instance from the Shell Group of companies. Further examples of Fischer-Tropsch derived gas oils are described in EP-A-0 583 836, EP-A-1 101 813, WO-97/14768, WO-97/14769, WO-00/20534, WO-00/20535, WO-01/11116, WO-01/11117, WO-01/83406, WO-01/83641, WO-01/83647, WO-01/83648 and US-A-6,204,426.

[0034] Suitably, in accordance with the present invention, the Fischer-Tropsch derived gas oil (ii) will consist of at least 90 % w/w, preferably at least 95 % w/w, of paraffinic components, preferably iso- and linear paraffins. The weight ratio of iso-paraffins to normal paraffins will suitably be greater than 0.3 and may be up to 12; most suitably it is from 2 to 6. The actual value for this ratio will be determined, in part, by the hydroconversion process used to prepare the gas oil from the Fischer-Tropsch synthesis product. Some cyclic paraffins may also be present.

[0035] By virtue of the Fischer-Tropsch process, a Fischer-Tropsch derived gas oil has essentially no, or undetectable levels of, sulphur and nitrogen. Compounds containing these heteroatoms tend to act as poisons for Fischer-Tropsch catalysts and are therefore removed from the synthesis gas feed. Further, the process as usually operated produces no or virtually no aromatic components. The aromatics content of a Fischer-Tropsch gas oil, as determined by ASTM D 4629, will typically be below 1 % w/w, preferably below 0.5 % w/w and more preferably below 0.1 % w/w.

[0036] The Fischer-Tropsch derived gas oil (ii) will typically have a density from 0.76 to 0.79 g/cm³ at 15 °C; a cetane number (ASTM D976) greater than 70, suitably from 74 to 82; a kinematic viscosity from 2.5 to 4.0, preferably from 2.9 to 3.7, centistokes at 40 °C; and a sulphur content of 5 ppmw (parts per million by weight) or less.

[0037] Preferably it is a product prepared by a Fischer-Tropsch methane condensation reaction using a hydrogen/carbon monoxide ratio of less than 2.5, preferably less than 1.75, more preferably from 0.4 to 1.5, and ideally using a cobalt containing catalyst. Suitably it will have been obtained from a hydrocracked Fischer-Tropsch synthesis product

(for instance as described in GB-2 077 289 B and/or EP-A-0 147 873), or more preferably a product from a two-stage hydroconversion process such as that described in EP-A-0 583 836 (see above). In the latter case, preferred features of the hydroconversion process may be as disclosed at pages 4 to 6, and in the examples, of EP-A-0 583 836.

[0038] In the fuel composition of the invention, component (ii) may be present in a concentration of up to 20 % v/v, preferably from 1 to 15 % v/v, more preferably from 2 to 12 % v/v, such as from 5 to 10 % v/v.

[0039] The Fischer-Tropsch derived naphtha fuel (iii) is a liquid hydrocarbon middle distillate fuel with a final boiling point of typically up to 220 °C or preferably of 180 °C or less, and which is a reaction product of a Fischer-Tropsch methane condensation process, such as for example the Shell Middle Distillate Synthesis described above. Its initial boiling point is preferably higher than 25 °C, more preferably higher than 35 °C. Its components (or the majority, for instance 95 % w/w or greater, thereof) are typically hydrocarbons having 5 or more carbon atoms; they are usually paraffinic.

[0040] The distillation properties of the naphtha fuel are comparable to those of gasoline. Despite this, naphtha fuel components of this type have not previously been used directly in gasoline fuel compositions because their octane numbers are too low, and have been incorporated instead into diesel fuel blends for instance for winter fuels.

[0041] As with the corresponding gas oils, Fischer-Tropsch derived naphtha fuels tend to be low in undesirable fuel components such as sulphur, nitrogen and aromatics. In the fuel composition of the present invention, the naphtha fuel component (iii) preferably has a density of from 0.67 to 0.73 g/cm³ at 15 °C and/or a sulphur content of 5 ppmw or less. It preferably contains 95 % w/w or greater of iso- and normal paraffins, preferably from 20 to 80 % w/w or greater of normal paraffins.

[0042] In the fuel composition of the invention, component (ii) may be present in a concentration of up to 20 % v/v, preferably from 1 to 15 % v/v, more preferably from 2 to 12 % v/v, such as from 5 to 10 % v/v. It is preferably the product of a SMDS process, preferred features of which may be as described above in connection with component (ii).

[0043] Any of the additional components (i) to (iii) may be pre-mixed with the gasoline base fuel, eg. prior to loading into the fuel tank of an automobile to be run on the fuel composition of the invention. Alternatively, and often preferably, they may be mixed with the base fuel *in situ* immediately prior to, or on, introduction of the fuel composition into an engine. By way of example, the additional component(s) may be mixed with the base fuel on board an automobile, for instance from separate storage vessels such as in the manner described by Olsson et al (*supra*) - such mixing may occur on introduction of the base fuel and additional component(s) into a combustion chamber of the engine, for instance by metering separate streams of the base fuel and additional component(s) directly into the fuel inlet system or combustion chamber via separate inlets. Alternatively the two components may be metered into a separate mixing chamber upstream of the fuel inlet system and/or combustion chamber.

[0044] An engine management system may be used to control switching between fuel supplies as loads change, for instance in response to accelerator pedal movement, allowing the engine to run on a fuel according to the invention at lower loads and thus extending its HCCI operating regime. In the case of *in situ* mixing, the engine management system may be used to control metering of gasoline fuel and additional component(s), from separate tanks, into a combustion chamber of the engine or into an upstream mixing chamber, in appropriate proportions. Here the tank(s) carrying the additional component(s) may be much smaller in capacity than that for the gasoline base fuel. In the case where a fuel according to the invention is stored in pre-mixed form, switching may then be between this and a conventional gasoline fuel also carried on board.

[0045] A second aspect of the present invention provides a method of operating a HCCI internal combustion engine, and/or an automobile or other machine which is driven by such an engine, which method involves introducing into a combustion chamber of the engine a fuel composition according to the first aspect. As described in connection with the first aspect of the invention, the fuel composition may be prepared *in situ* on board a machine to be driven by the engine, immediately before or on introduction of the fuel composition into the combustion chamber.

[0046] According to a third aspect of the invention there is provided a HCCI internal combustion engine in combination with a source of a fuel composition according to the first aspect of the invention, and/or with sources of (a) a gasoline base fuel and (b) one or more of the additional components (i) to (iii). In particular there is provided an automobile or other machine incorporating such an engine in combination with the relevant fuel source(s). Again, the term "HCCI internal combustion engine" is intended to encompass any internal combustion engine which either is, or is capable of, operating in HCCI mode.

[0047] The engine and fuel source(s) are preferably provided in combination with control means by which a fuel composition in accordance with the invention may be supplied, in appropriate quantities and with appropriate proportions of gasoline base fuel and additional component(s), to a combustion chamber of the engine, ideally at times when HCCI operation of the engine might benefit from a fuel composition according to the invention.

[0048] Where the system incorporates separate sources of a gasoline base fuel and one or more of the additional components (i) to (iii), the capacity of any "secondary" vessel for storage of the additional component(s) is preferably 50 % or less of, more preferably 20 % or less of, still more preferably 10 % or 5 % or 2 % or less of that of the vessel in which the base fuel is stored. A suitable capacity for a secondary storage vessel for a component of type (i), for

instance, might be from 0.5 to 5 litres, preferably from 0.5 to 3 litres, such as about 1 litre.

[0049] A fourth aspect of the present invention provides the use of one or more of the additional components (i) to (iii) above in a gasoline fuel composition for use in a HCCI internal combustion engine, preferably for the purpose of improving the auto-ignition properties of the fuel composition.

[0050] By "gasoline fuel composition" in this context is meant a fuel composition which comprises a gasoline base fuel, typically a major proportion (eg, 80 % v/v or more, preferably 90 % v/v or more, most preferably 95 % or 99 % or 99.5 % v/v or more) of the gasoline base fuel.

[0051] "Use" of the additional component(s) in a fuel composition means incorporating the component(s) into the composition, typically as a blend (ie, a physical mixture). This may be done before the composition is introduced into an engine or, as described above, may involve some form of *in situ* mixing of a gasoline base fuel and the additional component(s) immediately prior to, or on, introduction of the fuel composition into a combustion chamber of the engine, for instance from separate storage vessels on board a machine to be driven by the engine.

[0052] An improvement in the auto-ignition properties of the fuel composition, and preferably therefore of its low load performance in a HCCI engine, should be as compared to the gasoline base fuel alone, and/or to the same composition but minus the additional component(s) (i) to (iii). It will typically be manifested by auto-ignition occurring earlier in the engine cycle when the engine is running on the fuel composition containing the additional component(s), at any given air/fuel ratio, compression ratio, inlet charge temperature and engine speed. Instead or in addition, it may be manifested by a lower value of BT_{min} and/or a higher value of λ_{min} (the minimum values of brake torque and air/fuel ratio respectively at which auto-ignition can be sustained) for any given set of operating conditions such as compression ratio, inlet charge temperature and engine speed. The performance of the engine at lower loads may thereby be greatly improved.

[0053] Such aspects of fuel and engine performance may be assessed for instance by running an engine, such as a single cylinder HCCI engine, on the fuel composition(s) in question and measuring the crank angle at which auto-ignition occurs at any given air/fuel ratio, for example as described in the examples below.

[0054] Improved auto-ignition may mean that for any given inlet charge temperature, the engine may be run (without mis-firing) with a lower compression ratio than if it were running on the gasoline base fuel and/or on a fuel composition which did not contain any of the components (i) to (iii). It may mean that for any given compression ratio, the inlet charge temperature does not need to be so high in order to maintain HCCI combustion without mis-firing.

[0055] In general, therefore, use of the additional component(s) according to the fourth aspect of the invention can extend the lower HCCI operating limits of an engine by allowing a leaner fuel mixture (ie, a higher air/fuel ratio) to be used to give a lower torque at any given speed. Thus if the engine is adapted to operate in two or more ignition modes, the operating range over which it can be run in HCCI mode can be extended by running it on a gasoline fuel composition containing the additional component(s).

[0056] A fifth aspect of the present invention provides a process for the preparation of a fuel composition, such as a composition according to the first aspect, which process involves blending a gasoline base fuel with one or more of the additional components (i) to (iii) defined above. Again the blending is ideally carried out with the aim of improving the auto-ignition properties of the fuel composition in a HCCI internal combustion engine. It may be carried out *in situ*, ie, immediately before, or on, introducing the fuel composition into a combustion chamber of an engine.

[0057] Preferred features of the second to the fifth aspects of the invention, in particular regarding the nature of the gasoline base fuel and the nature and quantities of the additional component(s) (i) to (iii), may be as described above in connection with the first aspect of the invention.

[0058] The present invention will be further understood from the following examples, which illustrate the effects of components (i) to (iii) on the performance of a gasoline fuel in a HCCI engine.

General

[0059] The following tests used a single-cylinder HCCI engine (compression ratio 10.3, bore 80.6 mm, stroke 86.0 mm, connecting rod length 140.7 mm, crank throw 44 mm, displacement volume 449 cm³) having a pent-roof combustion chamber, four valves and two straight intake ports, mounted on a dynamometer. Valve timings were as listed in Table 1.

Table 1

inlet valve open (IVO)	450 CAD ATDC*
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*CAD = crank angle degree; ATDC = after top dead centre. Fuel was injected into the ports using an electronic injector system, the timing and quantity of injection being independently variable. Fuel was injected at the top dead centre (TDC) of the compression stroke to enable full vapourisation. The inlet air was at room temperature, ie, around 15 °C. The normalised air/fuel ratio, λ , was measured by analysing the oxygen content of the exhaust gases using an NTK MO1000™ analyser (when the mixture strength is stoichiometric, $\lambda = 1$, whereas for a fuel lean mixture, $\lambda > 1$). In-cylinder pressure was measured using a Kistler™ pressure transducer.

Table 1 (continued)

Inlet valve close (IVC)	580 CAD ATDC
Exhaust valve open (EVO)	150 CAD ATDC
Exhaust valve close (EVC)	260 CAD ATDC

[0060] The tests involved supplying the engine with either a gasoline base fuel A, having the properties listed in Table 2:

Table 2

Density @ 15 °C (g/cm ³) (ISO 3675:93)	0.733
Research octane number (RON) (EN 25164)	95.2
Motor octane number (MON) (EN 25163)	87.1
Distillation (% evap) (ISO 3405:88) :	
IBP (° C)	38
FBP (° C)	169
E70	26
E100	49.5
E120	71
C	6.76
H	12.59
O	0
Iso- + n-paraffins (% v/v)	61.6
Olefins (% v/v)	3.51
Aromatics (% v/v)	31.9
Oxygenates (% v/v)	0

or a blend of the base fuel with one of the additives i, ii or iii detailed below.

[0061] The engine was run at a fixed speed of 1500 rpm, full throttle opening, and the coolant and oil temperatures were fixed at 85 °C and 100 °C respectively.

[0062] The engine was firstly warmed up with the base gasoline fuel A, using spark ignition, until the coolant and oil temperatures stabilised at their fixed values. The fuelling level was adjusted until λ reached 1.0. Ignition was then switched off and the engine started running in HCCI mode.

[0063] The pressure signal was recorded using a storage oscilloscope, from which was determined the crank angle CA_i at which auto-ignition occurred in HCCI combustion. CA_i for the base fuel A was assumed to be zero and CA_i for the fuel blends was therefore expressed in terms of crank angles before this arbitrary zero.

[0064] The fuel flow rate was slowly reduced and the engine was run at a leaner condition of $\lambda=1.1$ to repeat the measurements. The fuel flow rate was further slowly reduced until the engine began to misfire and eventually stopped because auto-ignition could no longer be sustained. The value of λ and of the brake torque just before this happened were recorded and represent the limiting conditions denoted by λ_{min} and BT_{min} respectively. A lower value for BT_{min} indicated improved performance.

[0065] At each change of fuel, the engine was flushed through with the new fuel for one minute with the fuel pump running and the return fuel drained from the engine. This minimised cross contamination between tests.

Examples 1

[0066] In these examples, the performance of the base fuel A was compared with that of blends of fuel A with additive i, which is the diesel ignition improver 2-ethyl hexyl nitrate (2EHN). Fuel blend B contained 99.8 % v/v of the base fuel and 0.2 % v/v 2EHN. Blend C contained 99.5 % v/v of the base fuel and 0.5 % v/v 2EHN.

[0067] The base fuel was also compared with a fuel blend D containing 90 % v/v of fuel A with 10 % v/v n-heptane,

as used in the HCCI dual fuel system disclosed by Olsson et al (*supra*). The results are shown in Table 3.

Table 3

		CA_i^* $\lambda = 1$	CA_i $\lambda = 1.1$	λ_{min}	BT_{min} (Nm)
Fuel A	Base gasoline	0.0	0.0	1.15	5.1
Fuel blend B	99.8 %v fuel A + 0.2 %v 2EHN	7.7	9.5	1.27	3.95
Fuel blend C	99.5 %v fuel A + 0.5 %v 2EHN	9.0	10.3	1.38	2.8
Fuel blend D	90 %v fuel A + 10 %v n-heptane	10.8	9.0	1.25	3.95

* CA_i is crank angle degrees before the time of auto-ignition for base fuel A

[0066] It can be seen that for both EHN-containing fuel blends B and C, auto-ignition occurs much earlier in the engine cycle compared to the base fuel A.

[0069] The blends B and C also have significantly lower values of BT_{min} and higher values of λ_{min} compared to the base fuel A. Thus the additive 2EHN appears to extend the lower HCCI operating limit by allowing a leaner fuel mixture to be run to give a lower torque at a given speed.

[0070] Moreover the improvement at a 2EHN treat rate of 0.2 % v/v compares favourably with that observed using n-heptane at a treat rate (10 % v/v) which is 50 times greater - see data for blends B and D in Table 3. Thus 2EHN is nearly 50 times as effective as n-heptane in improving auto-ignition performance. This means a significant reduction in the tank capacity necessary for the additive to be carried in a separate tank on board a vehicle, for *in situ* mixing with a gasoline base fuel.

Examples 2

[0071] In these examples, the performance of the base fuel A was compared with that of blends of fuel A with additive II, which is a Fischer-Tropsch derived gas oil made by the Shell Middle Distillate Synthesis (SMDS) as described above. Fuel blend E contained 90 % v/v of the base fuel and 10 % v/v of the SMDS gas oil. Blend F contained 95 % v/v of the base fuel and 5 % v/v gas oil.

[0072] The gas oil II had been obtained from a Fischer-Tropsch (SMDS) synthesis product via a two-stage hydro-conversion process analogous to that described in EP-A-0 583 836. Its properties are listed in Table 4, and the test results in Table 5.

Table 4

Density @ 15 °C (g/cm ³)	0.7842
Distillation:	
IBP (°C)	212.5
10 %	248
20 %	264
30 %	277.5
40 %	290.5

Table 4 (continued)

50 %	300.5
60 %	309
70 %	316
80 %	327
90 %	332
95 %	338
FBP	344
Kinematic viscosity @ 40 °C (centistokes)	3.457

Table 5

		CA _i $\lambda = 1$	CA _i $\lambda = 1.1$	λ_{min}	BT _{min} (Nm)
Fuel A	Base gasoline	0.0	0.0	1.15	5.1
Fuel blend E	90 %v fuel A + 10 %v SMDS gas oil	9.9	10.4	1.23	4.2
Fuel blend F	95 %v fuel A + 5 %v SMDS gas oil	1.4	1.6	1.17	4.6

Again for both fuel blends E and F, auto-ignition occurs earlier in the engine cycle compared to the base fuel A. The blends also give significantly lower values of BT_{min} and higher values of λ_{min} compared to the base gasoline. Thus the SMDS gas oil additive extends the lower HCCI operating limit by allowing a leaner fuel mixture to be run to give a lower torque at a given speed.

Examples 3

[0073] Here the performance of the base fuel A was compared with that of blends of fuel A with additive III, which is a Fischer-Tropsch derived naphtha made by the Shell Middle Distillate Synthesis (SMDS) as described above. This naphtha fuel had a density @ 15 °C of 0.590 g/cm³, an initial boiling point of 43 °C and a final boiling point of 166 °C. Fuel blend G contained 90 % v/v of the base fuel and 10 % v/v of the SMDS naphtha. Blend H contained 95 % v/v of the base fuel and 5 % v/v SMDS naphtha.

[0074] The results are shown in Table 6.

Table 6

		CA _i λ = 1	CA _i λ = 1.1	λ _{min}	ET _{min} (Nm)
Fuel A	Base gasoline	0.0	0.0	1.15	5.1
Fuel blend G	90 %v fuel A + 10 %v SMDS naphtha	3.8	2.5	1.19	4.5
Fuel blend H	95 %v fuel A + 5 %v SMDS naphtha	2.7	2.2	1.17	4.65

For both naphtha-containing blends auto-ignition occurs earlier in the engine cycle than for the base fuel A. The blends also have significantly lower values of BT_{min} and higher values of λ_{min} compared to the base fuel A. Thus the SMDS naphtha additive again appears to extend the lower HCCI operating limits of the engine.

Claims

1. A fuel composition comprising a gasoline base fuel and one or more additional components selected from the group consisting of (i) a diesel fuel ignition improver, (ii) a Fischer-Tropsch derived gas oil and (iii) a Fischer-Tropsch derived naphtha fuel.
2. A fuel composition according to claim 1, wherein the diesel fuel ignition improver (i) comprises one or more reagents selected from the group consisting of:
 - a) organic nitrates of the general formula R¹-O-NO₂, or nitrites of the general formula R¹-O-NO, where R¹ is a hydrocarbyl group optionally containing an ether group;
 - b) organic peroxides and hydroperoxides, of the general formula R²-O-O-R³, where R² and R³ are each independently either hydrogen or a hydrocarbyl group; and
 - c) organic peracids and peresters, of the general formula R⁴-C(O)-O-O-R⁵, where R⁴ and R⁵ are each independently either hydrogen or a hydrocarbyl group.
3. A fuel composition according to claim 2, wherein the diesel fuel ignition improver (i) comprises an alkyl or cycloalkyl nitrate, in particular 2-ethyl hexyl nitrate.
4. A fuel composition according to any one of the preceding claims, wherein the diesel fuel ignition improver (i) is present at a concentration of up to 1 % v/v.
5. A fuel composition according to any one of the preceding claims, wherein the Fischer-Tropsch derived gas oil (ii) and/or the Fischer-Tropsch derived naphtha fuel (iii) is present at a concentration of up to 20 % v/v.
6. A method of operating an internal combustion engine in the HCCI mode, which method involves introducing into a combustion chamber of the engine a fuel composition according to any one of the preceding claims.
7. A HCCI internal combustion engine in combination with a source of a fuel composition according to any one of claims 1 to 5, and/or with sources of (a) a gasoline base fuel and (b) one or more of the additional components (i) to (iii) as defined in any one of claims 1 to 5.
8. A process for the preparation of a fuel composition, which process involves blending a gasoline base fuel with one or more of the additional components (i) to (iii) as defined in any one of claims 1 to 5.

9. The use of one or more components selected from the group consisting of (i) a diesel fuel ignition improver, (ii) a Fischer-Tropsch derived gas oil and (iii) a Fischer-Tropsch derived naphtha fuel, in admixture with a gasoline base fuel, in a gasoline fuel composition for use in a HCCI internal combustion engine, preferably for the purpose of improving the auto-ignition properties of the fuel composition.

10. A process or use according to claim 8 or claim 9, wherein the gasoline base fuel and the additional component(s) are mixed *in situ* immediately prior to, or on, introduction of the fuel composition into a combustion chamber of a HCCI engine.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 02 25 4129

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	<p>DOWNES ET AL: "THE EFFECTS OF ADDITIVES ON THE OCTANE NUMBER AND CETANE NUMBER OF GASOLINES"</p> <p>JOURNAL OF THE INSTITUTE OF PETROLEUM, LONDON, GB, vol. 515, no. 52, 1 November 1966 (1966-11-01), pages 331-346, XP002075689</p> <p>ISSN: 0020-3068</p>	1-4,6-9	<p>C10L1/08</p> <p>C10L1/22</p> <p>C10L1/18</p> <p>C10L1/16</p>
Y	* the whole document *	8,10	
X	<p>EP 0 879 871 A (ETHYL CORP)</p> <p>25 November 1998 (1998-11-25)</p> <p>* page 6, line 42 - line 43; claims 1,5,10 *</p>	1-4,8	
X	<p>US 2 324 779 A (KASS CHARLES B)</p> <p>20 July 1943 (1943-07-20)</p> <p>* example *</p>	1-4,8	
X	<p>GB 1 152 389 A (KAILASH CHANDER SALOOJA)</p> <p>14 May 1969 (1969-05-14)</p> <p>* examples 1,2 *</p>	1-4,8	<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p> <p>C10L</p>
Y	<p>US 2002/026926 A1 (AKINYEMI OMOWOLEOLA C ET AL) 7 March 2002 (2002-03-07)</p> <p>* paragraph [0189]; claim 1 *</p>	8,10	
-The present search report has been drawn up for off-claims			
Place of search		Date of completion of the search	Examiner
MUNICH		4 September 2002	Keipert, D
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>I : document cited for other reasons</p> <p>A : member of the same patent family, corresponding document</p>			

EPQ FORM 1533 (03/02) (P.4/2011)



European Patent
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Application Number

EP 02 25 4129

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1 (part), 2 (part), 3, 4, 6 (part), 7 (part), 8 (part),
9 (part), 10 (part)



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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 02 25 4129

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1(part), 2(part), 3, 4, 6(part), 7(part), 8(part), 9(part), 10(part)

- 1.1. Claims: 1(part), 2(part), 3, 4

A fuel composition comprising a gasoline base fuel and one or more reagents selected from the group consisting of organic nitrates of the general formula $R1-O-NO_2$, or nitrites of the general formula $R1-O-NO$, where $R1$ is a hydrocarbyl group.

- 1.2. Claim : 6(part)

A method of operating an internal combustion engine in the HCCI mode, which method involves introducing into a combustion chamber of the engine a fuel according to sub-invention 1.1.

- 1.3. Claim : 7(part)

An HCCI internal combustion engine in combination with a source of a fuel composition according to sub-invention 1.1.

- 1.4. Claims: 8(part), 10(part)

A process for the preparation of a fuel composition according to sub-invention 1.1.

- 1.5. Claim : 9(part)

The use of one or more components selected from selected from the group consisting of organic nitrates of the general formula $R1-O-NO_2$, or nitrites of the general formula $R1-O-NO$, where $R1$ is a hydrocarbyl group, in admixture with a gasoline base fuel, in a gasoline fuel composition for use in an HCCI internal combustion engine.

2. Claims: 1(part), 2(part), 4, 6(part), 7(part), 8(part), 9(part), 10(part)

A fuel composition comprising a gasoline base fuel and one or more organic peroxides and hydroperoxides, of the general formula $R2-O-O-R3$, where $R2$ and $R3$ are each independently either hydrogen or a hydrocarbyl group.



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LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 02 25 4129

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

3. Claims: 1(part), 2(part), 4, 6(part), 7(part), 8(part),
9(part), 10(part)

A fuel composition comprising a gasoline base fuel and one or more organic peracids or peresters, of the general formula $R_4-C(O)-O-O-R_5$, where R_4 and R_5 are each independently either hydrogen or a hydrocarbyl group.

4. Claims: 1(part), 5, 6(part), 7(part), 8(part), 9(part),
10(part)

A fuel composition comprising a gasoline base fuel and a Fischer-Tropsch derived gas oil.

5. Claims: 1(part), 5, 6(part), 7(part), 8(part), 9(part),
10(part)

A fuel composition comprising a gasoline base fuel and a Fischer-Tropsch derived naphtha fuel.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 4129

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

04-09-2002

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EP's FORM 1043

For more details about this annex : see Official Journal of the European Patent Office, No. 12/92